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(54) PRODUCTION OF ETHYLENE DICHLORIDE

(71) We, ALLIED CHEMICAL CORPORATION, a Corporation organised and existing under the laws of the State of New York, United States of America, of 1411 Broadway, New York, New York 10018, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved process for preparing ethylene dichloride (1,2 - dichloroethane) by the liquid phase reaction between ethylene and chlorine. Ethylene dichloride has many uses, for example as the raw material in the manufacture of vinyl chloride.

Most present-day commercial processes for the production of ethylene dichloride are based on the liquid phase reaction between ethylene and chlorine in a reaction medium of liquid ethylene dichloride. The reaction between chlorine and ethylene is highly exothermic and the temperature in the reaction medium must be controlled to prevent the formation of undesirable substitution reaction products.

In the production of vinyl chloride by pyrolysis of ethylene dichloride, certain chlorinated contaminants such as ethyl chloride and 1,1,2 - trichloroethane have detrimental effects, even when only minute quantities are present. For this reason, it has generally been necessary to subject ethylene dichloride to costly purification steps before using it for the production of vinyl chloride. The product of the process of the present invention, however, is essentially free from such chlorinated substitution reaction products and can therefore be used directly for the production of high quality vinyl chloride by pyrolysis, without further purification.

United States Patent No. 2,393,367 discloses a process for the preparation of ethylene dichloride in which process ethylene and chlorine are introduced into a water-cooled reactor containing ethylene dichloride with a small amount of ferric chloride as a sub-

stitution reaction depressant (to reduce the formation of higher chlorinated products). The reactor employed has a plurality of internal tubes which carry a cooling agent to maintain the reaction medium at a temperature of about 40°C., which is well below the boiling point of ethylene dichloride (83.3°C.). Even in the presence of ferric chloride, at least about 0.5% of the chlorine forms undesirable higher chlorinated products, and the ethylene dichloride produced by this process therefore requires purification before it is suitable for use as a raw material for the production of vinyl chloride, or in other industrial processes.

United States Patent No. 2,929,852 also discloses a process involving the liquid phase reaction between ethylene and chlorine in an ethylene dichloride reaction medium. Direct temperature control is achieved by utilising the exothermic heat of reaction to vapourise that portion of the ethylene dichloride which becomes the purified product. The temperature of the reaction medium is held between 80 and 120°C. at pressures of 0 to 25 lbs. per square inch gauge (psig). The vapourised portion of the ethylene dichloride reaction medium is conducted to a rectification column, ethylene dichloride is separated from the higher chlorinated reaction products and the ethylene dichloride product is removed in liquid phase from the rectification zone. The product of this process, although of greater purity than that obtainable from the process of United States Patent No. 2,393,367, is less pure than the product of the process of the present invention.

In the process of the present invention the exothermic reaction is controlled by circulation of the reaction medium through an external heat exchanger in conjunction with the removal of heat from the reaction zone by the continuous vapourisation of a portion of the reaction medium. In this way the temperature in the reaction zone is maintained at the boiling point of the reaction mixture; this temperature is generally 83°C. or higher, depending on the quantity of high boilers pre-

5 sent. The process involves the circulation of the hot reaction medium from the bottom to the top of the reaction zone, then to the top of the cooling or heat extraction zone, then from the top to the bottom of the heat extraction zone and then back into the bottom of the reaction zone, thus describing a continuous cyclic loop; the liquid circulates in this way without the use of pumps or other mechanical means.

10 Accordingly, the present invention provides a process for the continuous production of ethylene dichloride by reaction of ethylene and chlorine in a liquid ethylene dichloride reaction medium, which process comprises

15 a) continuously introducing ethylene and chlorine, in relative proportions such that the amount of ethylene is at least the stoichiometric amount required to produce ethylene dichloride, into a vertically disposed reaction zone containing the reaction medium, the points of introduction of ethylene and chlorine being at or near the bottom of the reaction zone, and maintaining the temperature in the reaction zone at the boiling point of the reaction mixture to effect an exothermic reaction between the ethylene and the chlorine and to induce upward movement of the liquid reaction medium in the reaction zone,

20 b) conducting the upwardly flowing liquid from a point at or near the top of the reaction zone to a point at or near the top of an externally cooled vertically disposed heat extraction zone to cool the liquid by heat exchange and to cause it to flow down the heat extraction zone,

25 c) conducting the cooled liquid from a point at or near the bottom of the heat extraction zone to a point at or near the bottom of the reaction zone such that a continuous circulation of the liquid between the reaction zone and the heat extraction zone is maintained without mechanical means, and

30 d) removing from the reaction zone ethylene dichloride-containing vapours formed by the heat of reaction of the ethylene and chlorine, and recovering ethylene dichloride from the vapours by condensation.

35 The process of the invention may be performed in apparatus as claimed in our co-pending application No. 45329/74 (Serial No. 1391092) [Our Folio A 19998] divided out of the present application.

40 In the process of the reaction, part of the exothermic heat of reaction, which would otherwise be expended in additional vapourisation of the reaction medium, is removed by the passage of the reaction medium through the heat exchanger. Control of the quantity of heat removed and accordingly, control of the rate of vapourisation can be achieved by varying the temperature and/or the amount of coolant passing through the heat exchanger.

45 A portion of the circulating reaction medium is preferably purged from the reaction system,

either continuously or periodically, in an amount sufficient to prevent a build-up of highly chlorinated substitution reaction products in the reaction medium. Although the quantity of such substitution reaction products produced by the process of the present invention is generally very low, urging is the only satisfactory way of removing the higher boiling products among them. If permitted to accumulate in the reaction medium, these undesirable by-products would eventually build up in such amounts that they would be carried over into the final product, which would then require further purification. Ethyl chloride and 1,1,2 - trichloroethane are particularly undesirable contaminants in an ethylene dichloride product which is to be used as the raw material for the production of vinyl chloride. Ethyl chloride, being a low boiling by-product (B. Pt. 12.3°C.) is generally vented along with any other non-condensibles, but 1,1,2 - trichloroethane being a relatively high boiling by-product (B. Pt. 113.5°C.) accumulates in the reaction medium. the amount of 1,1,2 - trichloroethane that can be tolerated in the reaction medium without jeopardizing the quality of the product ethylene dichloride depends on the efficiency of the rectification section, as will be discussed below; thus a higher weight percent of this undesirable by-product can be tolerated where the rectification section chosen is highly efficient.

The amount of liquid purged is preferably such that the total amount of undesirable by-products constitutes less than 10%, preferably less than 5% of the reaction medium. In general the amount of liquid removed should be such that 1,1,2 - trichloroethane is removed from the reaction medium at a rate equal to at least that at which it is produced as a by-product. The ethylene dichloride in this purged material can subsequently be recovered by distillation, and recycled.

50 In the preferred embodiment of the process of our invention, the ethylene dichloride vapours from the reactor are conducted to a rectification section with a fractional distillation zone. The ethylene dichloride vapour which leaves the rectification section is condensed and the liquid ethylene dichloride is separated from the small quantity of non-condensable side reaction products which are formed. Generally, the greater portion of the condensed ethylene dichloride is returned to the fractional distillation zone as reflux; preferably the weight ratio of condensed ethylene dichloride recycled to the fractional distillation zone to ethylene dichloride not recycled is from 0.5:1 to 6:1, and the balance is withdrawn as high purity ethylene dichloride product. In this preferred embodiment a portion of the circulating liquid reaction medium whose weight is from 1 to 10% of the weight of ethylene dichloride not recycled to the

fractional distillation zone is continuously or periodically removed from the reaction system.

5 The conditions used in the process of the invention are such that circulation of the liquid reaction medium occurs without the use of a pump or other mechanical means. This circulation is caused by the "thermo-siphon" effect (whereby the heated liquid at
10 the bottom of the reaction zone expands and flows upwardly and is replaced by cooled liquid from the heat extraction zone) and is assisted by the gas-lift effect induced by the introduction of the reactants, the heat of
15 reaction and the bubbles of vapour produced thereby.

The use of an external heat extraction zone not only controls the rate of vapourisation, but is also indirectly responsible for the intimate
20 mixing of ethylene and chlorine which is essential for the production of high purity ethylene dichloride. The reaction between the chlorine and ethylene to form ethylene dichloride is believed to take place at the gas-
25 liquid interface, while the side reactions are thought to take place in the gas phase. For this reason, good dispersion of the reactants, which is associated with a relatively large area of gas-liquid interface, is important for
30 a high ethylene dichloride yield coupled with a low yield of the undesirable side reaction products.

As already mentioned, the ethylene/chlorine reaction is highly exothermic. When
35 the reactants are mixed in a reaction vessel without an external heat exchange zone, large bubbles of vapour are formed as the vapour pressure of the mixture reaches ambient pressure. Such large bubbles provide relatively
40 little gas-liquid interface throughout the reaction medium, and therefore a relatively large yield of undesired side reaction products is obtained. In comparison, the circulation of liquid made possible by the use of the
45 external heat exchanger and the good dispersion that results therefrom, provides a preponderance of very small bubbles of vapour. Consequently, a large area of gas-liquid interface is obtained since the surface area of a
50 large number of small bubbles is much greater than the surface area of fewer large bubbles of equivalent volume.

The temperature in the reaction zone is the boiling point of the circulating liquid reaction
55 medium. At atmospheric pressure, the boiling point generally ranges from 83.3°C. (the boiling point of pure ethylene dichloride), to higher temperatures depending on the quantity of high boilers present. Typical reaction temperatures are 83.3 to 90°C. It is, of course,
60 possible to carry out the reaction at pressures somewhat above or below atmospheric pressure with a corresponding shift in the boiling range, but atmospheric pressure is preferred.
65 There is also a correlation between the amount

of liquid purged and the boiling point of the reaction medium; if only a small amount of the reaction medium is purged, the quantity of high boiling impurities in the reaction medium will gradually increase, with a corresponding increase in the boiling point of the mixture. 70

Ferric ions (e.g. in the form of ferric chloride) can be added to the reaction medium as a catalyst to depress the reaction rate of the substitution reactions. Fe^{+++} should be present in the reaction medium to the extent of at least 50 parts per million by weight (ppm), preferably 500—2000 ppm. Iron or steel equipment can be used for the reaction, in which case a trace of iron will generally be picked up by the reaction medium as a result of superficial corrosive action. If the ferric ion in the reaction medium produced by such corrosive action is less than 500 ppm, a quantity of ferric chloride may be added to bring the Fe^{+++} content to the preferred level of at least 500 ppm. 75 80

A small amount of oxygen can also be added to the reaction mixture to further inhibit by-product formation. Oxygen is particularly effective in inhibiting the formation of 1,1,2-trichloroethane. The oxygen is preferably added with the chlorine in an amount of 0.5% by weight, based on the weight of chlorine. In place of pure oxygen, air may be introduced with the chlorine in an amount sufficient to provide an equivalent percentage of oxygen. 85 90 95

In the process of the invention the reactants must be supplied to the circulating ethylene dichloride reaction medium in at least the stoichiometric amounts required to produce ethylene dichloride, but it is preferred to use a stoichiometric excess of ethylene to reduce the tendency for the formation of higher chlorinated by-products. The preferred mole ratio of Cl_2 to C_2H_4 is at least 0.4:1, especially 0.90:1 to 0.95:1. 100 105

The process of the present invention can be conducted in a reactor provided with a rectification or fractionating zone. The rectification or fractionating zone may comprise any fractionating column designed to provide good liquid-vapour contact; the use of such a column increases the purity of the ethylene dichloride vapour by separating and recycling to the reactor any high boiling by-products produced by the reaction. The equipment should have reasonable resistance to corrosion by the reactants and reaction products; steel equipment is generally satisfactory. The rectification zone of the reactor may comprise a series of bubble cap trays or sieve plates, or it may comprise a column packed with Rashig rings, saddles or other suitable packing normally employed in rectification equipment. The purity of the product can be improved by increasing the height of the rectification zone. 110 115 120 125

The process of the invention will be further 130

described with reference to the accompanying drawing which diagrammatically illustrates equipment which may be employed in carrying out the process.

- 5 A reactor 1 is provided with a heat extraction zone or heat exchanger 3, through which liquid reaction medium may circulate by entering through conduit 5, and returning through conduit 7. Conduits 5 and 7 must
- 10 have effective inside diameters sufficiently large to permit adequate circulation of the reaction medium through the cyclic system formed by reactor 1, heat exchanger 3, and the interconnecting conduits 5 and 7. In order
- 15 to permit good circulation of the reaction medium the effective cross-sectional area of the heat exchanger is desirably at least equal to the cross-sectional area of the conduits, and the cross-sectional area of each of the con-
- 20 duits is preferably not less than about 2% of the cross-sectional area of the reaction zone. Preferably, the cross-sectional area of each of the conduits is about 15 to 100% of the effective cross-sectional area of the reaction zone.
- 25 Both conduits should be positioned entirely below the surface of the reaction medium when the equipment is operating; one conduit (5) connects reactor 1 and heat exchanger 3 at points near and just below the liquid surface, and the other conduit (7) connects reactor 1
- 30 and heat exchanger 3 at points in the lower portions of the reactor and heat exchanger. In the preferred embodiment, heat exchanger 3 is water cooled, the cooling water inlet and outlet being shown as 9 and 11 respectively.
- 35 The lower portion of reactor 1 comprises the reaction zone and is provided with an inlet 13 for raw material ethylene, and an inlet 15 for chlorine gas preferably containing about
- 40 0.5% by weight of oxygen (or a quantity of air sufficient to provide this quantity). Outlet 17 at a low point in the reactor system is provided for purging the system.
- 45 The level of the ethylene dichloride reaction medium is maintained at 19 by level-sensing device 21 which operates valve 23, thus controlling the amount of ethylene dichloride product which is continuously withdrawn at 25.
- 50 Reactor 1 is also provided at its upper end with a rectification section 27, from the top of which the ethylene dichloride and any low boiling substitution reaction products leave as vapours through riser 29 and enter the upper vestibule of down-coming condenser 31. Cool-
- 55 ing water is admitted to the jacket of condenser 31 through inlet 33 and outlet 35. The condensate and non-condensibles leaving the condenser enter separator 37 from which the non-condensibles are vented through vent line
- 60 39. At the separator, the condensate is split into two streams, one stream being returned through lute 41 and sparger 43 to the top of the rectification section, as reflux, and the other stream, passing through control valve
- 65 23, leaving at point 25 as purified ethylene

dichloride. The opening or closing of valve 23, either manually or automatically in response to signals from level-sensing device 21 maintains the liquid level in the reactor at 19 by controlling the product flow at 25 or 49 and thus the amount of reflux (generally the larger portion of the condensate), through lute 41 to sparger 43 and column 27. This action is facilitated when overflow line 41 extends a short distance up into separator 37 and is protected from the direct stream from condenser 31 by off-set positioning, by a protecting hood, a crooked end or other means. For example, if level 19 drops below a pre-selected point, sensing means 21 causes valve 23 to partially close. More condensate then accumulates in separator 37 and overflows through lute 41 to column 27, thence back to reactor 1, raising the liquid level at 19. If the liquid level 19 rises above the pre-selected point, sensing means 21 causes valve 23 to open further. This increases the rate of product withdrawal, and decreases the amount of reflux (condensate return to the reactor), thereby lowering the liquid level as the distillation progresses. The liquid level chosen is generally several inches above the upper interconnection between the reactor and heat exchanger to insure uninterrupted circulation of the liquid through the cyclic system. When the reactants are fed at a constant rate through lines 13 and 15, the amount of condensate from condenser 31 can be controlled by varying the amount of, or the temperature of, the coolant applied to the jacket of heat exchanger 3. Decreasing the rate of flow of the coolant, or increasing its temperature reduces the quantity of heat being removed from the reaction mixture, so that more heat is available for vapourising the product and reaction medium, thus increasing the total amount of condensate. The reflux ratio can therefore be governed by the degree of cooling provided by the external heat exchanger 3.

The ethylene dichloride product obtained at point 25 is of excellent quality for the production of vinyl chloride by pyrolysis, but it may contain a trace of hydrogen chloride which might be objectionable for general sales. This trace of HCl can be scrubbed out by passing the product through line 45 to packed column 47 countercurrent to an incoming stream of ethylene which enters at 48. HCl-free, high purity, ethylene dichloride is withdrawn at 49 and minor amounts of hydrogen chloride carried by the ethylene feed to reactor 1 would eventually be vented at line 39.

The preparation of ethylene dichloride by the process of the invention may be carried out as follows: Reactor 1 and attached heat exchanger 3 are filled with dry ethylene dichloride to level 19, the liquid level being maintained by level controller 21. Ferric chloride is added to this reaction medium to

provide between 500 and 2000 ppm of iron based on the total weight of reaction medium. The system is swept with ethylene; ethylene is then slowly sparged into the bottom of reactor 1 through line 13, and chlorine gas containing about 0.5% oxygen or an amount of air to provide a corresponding amount of oxygen is sparged through line 15. The ethylene is added in slight excess, the mole ratio of chlorine being 0.90 to 0.95 per mole of ethylene. The addition of the reactants is continued, gradually increasing the rate, until the reaction medium reaches its boiling point (83.3°C. or higher, depending on the quantity of high boiling impurities that are present). The rate of addition of the reactants, and the amount of cooling water to heat exchanger 3 are adjusted so as to obtain adequate reflux without flooding the rectification zone 27 or exceeding the capacity of condenser 31. At point 17 in the reaction system, a portion of the reaction medium equal to 1 to 10% by weight of the weight of ethylene dichloride removed at 25 is continuously purged. The precise rate of purge is adjusted to that which maintains the amount of undesirable highly chlorinated substitution reaction products in the reaction medium at a satisfactory low level. The purged ethylene dichloride can be recovered by distillation.

The ethylene dichloride product obtained by the process of the invention can be diverted directly to cracking furnaces if it is to be used for vinyl chloride production by pyrolysis. If a product free from HCl is desired, the product from 23 may be passed downwardly through packed column 47 countercurrent to a flow of incoming ethylene, which is diverted through said column en route to reactor 1. The stream of ethylene sweeps the ethylene dichloride essentially free of HCl. The negligible amount of HCl picked up by the ethylene is not detrimental to the C_2H_4/Cl_2 reaction and essentially all of it is removed with the non-condensibles at 37, then vented through vent line 39.

The process of the invention is further illustrated by Examples 1 and 2. Examples 3 and 4 are comparative Examples.

EXAMPLE 1

Small scale equipment is set up corresponding to the arrangement shown in the accompanying drawing. The reactor consists of a length of iron pipe 3' 4" long, having an inside diameter (ID) of 4". Gas inlets enter the reactor near the bottom and these are equipped with sparging means for the dispersion of the reactant gases. A drain cock is also provided at the bottom for purging the system. A jacketed iron tubular heat exchanger having an overall diameter of 6" and a length of 3 1/2 feet is positioned parallel and adjacent to the reactor. The heat exchanger is connected to the reactor by two 2" ID iron

pipes at two points. One such pipe is centred at a point 4" from the bottom of the reactor, and extends horizontally to the outlet vestibule of the heat exchanger and the other pipe is centred at a point 4" from the top of the reactor and extends horizontally to the inlet vestibule of the heat exchanger, thus forming a path for the cyclic flow of reaction medium. The reactor system is charged with 14 litres of ethylene dichloride (as the reaction medium) bringing the liquid level just above the upper inter-connection between the reactor and heat exchanger. A small amount of ferric chloride is added (25 grams, anhydrous basis) to provide a Fe^{+++} content of about 500 ppm based on the weight of the ethylene dichloride charge. Before any chlorine is added, the system is first purged with ethylene as a safety measure, since, as previously emphasized, the reaction between ethylene and chlorine is highly exothermic and the presence of air in the system at the start might cause an explosion (an inert gas can be used at this point if desired.) The feed ethylene, chlorine and oxygen (air) are accurately measured by means of suitable flow meters. The following rates of addition are employed:

Chlorine, 60 grams per minute

Ethylene, 26.1 grams per minute

Air, 0.58 grams per minute

This represents a mole ratio of chlorine to ethylene of 0.91 to 1.0. The operation is carried out essentially at atmospheric pressure. The reactor temperature is maintained at 84°C., and the ethylene dichloride product is withdrawn at the rate of about 75 grams per minute, while about 4 grams per minute of reaction mixture are purged from the reactor system, thus maintaining the quantity of substitution reaction products which may accumulate in the reaction medium at a low and essentially constant level.

The reflux ratio is maintained at about 5.4 to 1.0. 96—99% of the chlorine is converted to ethylene dichloride.

The purity of the product obtained is found to be 99.80% ethylene dichloride, which is exceptionally high for this material.

EXAMPLE 2

Example 2 is carried out in exactly the same way as Example 1, except that no ferric chloride is added, since the reaction medium from Example 1, which already contains Fe^{+++} is reused. Furthermore, a slight corrosive attack of the wall of the iron reactor increases the Fe^{+++} content to some extent. The reactor temperature is maintained at 86°C. Feed rates, reflux ratio, and product and purge rates are the same. The purity of the product is 99.74%.

EXAMPLE 3 (comparative)

Example 3 is carried out in exactly the same way as Example 1, with the sole excep-

tion that the conduits (5 and 7) to the external heat exchanger are blanked off. Feed rates, reactor temperature, reflux ratio, ferric iron concentration and product and purge rates are the same. 96—98% of the chlorine is converted to ethylene dichloride. The product is found to contain 99.36% ethylene dichloride. It will be noted that there is a decrease in product purity of about 0.44% when external means of cooling, with the associated circulation of the reaction medium, are not provided.

EXAMPLE 4 (comparative)

Example 4 is carried out in exactly the same way as Example 3. No make-up ferric chloride is required, as an Fe^{+++} content of 500 to 1000 ppm is already present (due to corrosion of the reactor). Feed rates, reactor temperature, reflux ratio, ferric iron concentration and product and purge rates are the same. 96—98% of the chlorine is converted to ethylene dichloride. The product is found to assay 99.17% ethylene dichloride. Again, it will be noted that a decrease in product purity occurs, this time amounting to almost 0.6% when external means of circulating and cooling the reaction medium are not provided.

The improvement in the purity of the ethylene dichloride product when circulation and external cooling of the reaction medium is provided, averages about 0.5%; this improvement is very significant. When a product of this degree of purity is used in the production of vinyl chloride by pyrolysis, the vinyl chloride obtained is of consistently good quality and the results are reproducible.

WHAT WE CLAIM IS:—

1. A process for the continuous production of ethylene dichloride by reaction of ethylene and chlorine in a liquid ethylene dichloride reaction medium, which process comprises

a) continuously introducing ethylene and chlorine, in relative proportions such that the amount of ethylene is at least the stoichiometric amount required to produce ethylene dichloride, into a vertically disposed reaction zone containing the reaction medium, the points of introduction of ethylene and chlorine being at or near the bottom of the reaction zone, and maintaining the temperature in the reaction zone at the boiling point of the reaction mixture to effect an exothermic reaction between the ethylene and the chlorine and to induce upward movement of the liquid reaction medium in the reaction zone,

b) conducting the upwardly flowing liquid from a point at or near the top of the reaction zone to a point at or near the top of an externally cooled vertically disposed heat extraction zone to cool the liquid by heat exchange and to cause it to flow down the heat extraction zone,

c) conducting the cooled liquid from a point at or near the bottom of the heat extraction zone to a point at or near the bottom of the reaction zone such that a continuous circulation of the liquid between the reaction zone and the heat extraction zone is maintained without mechanical means, and

d) removing from the reaction zone ethylene dichloride-containing vapours formed by the heat of reaction of the ethylene and chlorine, and recovering ethylene dichloride from the vapours by condensation.

2. A process according to claim 1 wherein a portion of the circulating liquid reaction medium is continuously or periodically removed from the reaction system.

3. A process according to claim 2 wherein the rate of removal of liquid reaction medium is such that 1,1,2-trichloroethane is removed from the reaction medium at a rate equal to at least that at which it is produced as a by-product.

4. A process according to any one of the preceding claims wherein in step d) the ethylene dichloride-containing vapours are fractionally distilled to remove lower boiling impurities before ethylene dichloride is separated from the vapours by condensation.

5. A process according to claim 4 wherein a portion of the condensed ethylene dichloride is recycled to the fractional distillation zone.

6. A process according to claim 5 wherein the weight ratio of condensed ethylene dichloride recycled to the fractional distillation zone to ethylene dichloride not recycled is from 0.5:1 to 6:1.

7. A process according to claim 5 or 6 wherein the weight ratio of condensed ethylene dichloride recycled to ethylene dichloride not recycled is controlled by varying the amount of coolant applied to the heat exchange zone.

8. A process according to claim 5 or 6 wherein the weight ratio of condensed ethylene dichloride recycled to ethylene dichloride not recycled is controlled by varying the temperature of coolant applied to the heat exchange zone.

9. A process according to any one of claims 5 to 8 wherein a portion of the circulating liquid reaction medium whose weight is from 1 to 10% of the weight of ethylene dichloride not recycled to the fractional distillation zone is continuously or periodically removed from the reaction system.

10. A process according to any one of the preceding claims wherein the reaction medium is maintained at substantially constant volume.

11. A process according to any one of the preceding claims wherein the temperature in the reaction zone is 83°C. or higher.

12. A process according to any one of the preceding claims which is performed at substantially atmospheric pressure.

13. A process according to claim 12 wherein

the temperature in the reaction zone is from 83.3 to 90°C.

5 14. A process according to any one of the preceding claims wherein the reaction medium contains at least 50 ppm by weight of ferric ions.

15. A process according to claim 14 wherein the reaction medium contains from 50 to 2,000 ppm by weight of ferric ions.

10 16. A process according to claim 15 wherein the reaction medium contains from 500 to 2,000 ppm by weight of ferric ions.

15 17. A process according to claim 15 wherein ferric chloride is added to the reaction medium to give a ferric ion concentration within the range of from 50 to 2,000 ppm by weight.

20 18. A process according to any one of the preceding claims wherein the chlorine to ethylene mole ratio is at least 0.4:1.

19. A process according to claim 18 wherein the chlorine to ethylene mole ratio is from 0.90:1 to 0.95:1.

25 20. A process according to any one of the preceding claims wherein the condensed ethylene dichloride product is passed through a packed column in counter-current to a flow

of ethylene to remove hydrogen chloride impurity from the ethylene dichloride and the hydrogen-chloride-containing ethylene thus obtained is used as starting material in the production of ethylene dichloride. 30

21. A process according to claim 1 for the continuous production of ethylene dichloride substantially as hereinbefore described. 35

22. A process according to claim 1 for the continuous production of ethylene dichloride substantially as described in Example 1 or 2.

23. A process according to claim 1 for the continuous production of ethylene dichloride which is carried out in apparatus as claimed in any one of the claims of application No. 45329/74 (Serial No. 1391092). 40

24. Ethylene dichloride produced by the process claimed in any one of the preceding claims. 45

25. Vinyl chloride prepared by pyrolysis of ethylene dichloride claimed in claim 24.

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1391091

COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale

